RADIATIVE EFFECTS OF CARBON DIOXIDE

IN THE UPPER STRATOSPHERE

by

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April, 1972

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Chairman, Departmental Committee on Graduate Students

Lindgren

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Submitted to the Department of Meteorology on 28 April 1972 in partial fulfillment of the requirements for the degree of Master of Science.

ABSTRACT

An approximate method of computing the infrared cooling due to the 15 µm band of carbon dioxide in the height region 30-60km is investigated. The method is based on the assumption of non-overlapping spectral lines, which is a valid assumption at all heights above 30km. The equivalent width of a line undergoing both pressure and Doppler broadening is evaluated by a simple approximation suggested by Curtis. The approximation is strictly correct for weak absorption at all heights and is an excellent approximation for intermediate absorption, but appears to be least accurate for strong lines around 50-60km.

Carbon dioxide band spectra are computed with the single line model for a range of mass paths and pressures, and the results are in excellent agreement with experimental studies and similar spectra computed with the quasi-random model.

Cooling rates are computed from the cooling to space approximation and range from 1.8 degrees per day near 30km to a maximum of 4.8 degrees per day near the stratopause.

Thesis Supervisor: Henry G. Houghton
Title: Professor of Meteorology
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I. Introduction

Empirical reasoning and approximate numerical methods traditionally have flourished in the field of atmospheric radiation. Some of these techniques may have bordered on the disreputable, but neither the physical magnitude of the atmosphere nor the accuracy to which the important parameters are known warrants a more exact treatment at the present time. Numerous authors have considered the radiative energy budget of the troposphere and lower stratosphere, and insofar as clouds and aerosols have been neglected, their results appear to be remarkably convergent.

The energy budget of the stratosphere and mesosphere is less well known, and substantial efforts have been made to cope with the problems encountered above 30km. One of the more serious complications in this region is the complicated profile that the spectral line assumes. No longer is it possible to approximate the line by a simple Lorentz profile, since Doppler broadening becomes increasingly more important as the pressure broadening effect diminishes. When the combined Doppler-Lorentz line shape is used in the traditional band models, the simplicity which made their use desirable in the lower atmosphere is lost. (Golden, 1967; Gille and Ellingson, 1968). Transmission functions derived from experimental data generally are not applicable above 30km. (Rodgers, 1964), and the remaining alternatives are integration over the Doppler-Lorentz profile or the use of more restrictive approximations.

This paper presents an extremely simple technique by which radiative temperature change can be evaluated with reasonable accuracy in the height range 30-60km. An undertaking of this nature is particularly desirable at the present time in view of the excellent Nimbus IV temperature data that the Oxford group has made available (Ellis et al., 1970) and its possible
II. Formulation of the problem.

The solution to Schwarzschild's equation for a plane, stratified atmosphere is well known:

\[
F_{A \nu}^+ (z) = B_{A \nu} \frac{d}{dz} \left[ \frac{1}{\tau_{A \nu} (z)} \right] d\nu
\]

where \( B_{A \nu} \) and \( \tau_{A \nu} \) are respectively the upward and downward fluxes of radiation at some reference level \( z \) and within some frequency interval \( A \nu \). The solution to Schr"{o}dinger's equation for a plane, stratified atmosphere is well known:

\[
F_{A \nu}^- (z) = \int \frac{1}{\tau_{A \nu} (z')} d\nu
\]

where \( F_{A \nu}^+ \) and \( F_{A \nu}^- \) are respectively the upward and downward fluxes of radiation at some reference level \( z \) and within some frequency interval \( A \nu \). The intensity transmission is

\[
\tau_{A \nu} (z, z') = \frac{2}{A \nu} \int E_{I_3} (\nu (z, z')) d\nu
\]

\( \tau_{A \nu} (z, z') \) is the monochromatic optical depth and \( E_{I_3} \) is the exponential integral needed for the angular integration. The intensity transmission is

\[
\tau_{A \nu} (z, z') = \frac{1}{A \nu} \int e^{-\tau_{A \nu} (z, z')} d\nu
\]

\( \tau_{A \nu} \) is given by

\[
\tau_{A \nu} = h \nu a
\]
where \( k_\nu \) is the absorption coefficient and \( a \) is the absorber amount. Evaluating (3) is a formidable task as it involves an integration over path length, frequency and line shape. The angular integration is often eliminated by means of the diffusivity factor \( S \), (Elsasser, 1942), such that

\[
\bar{I}_{\nu\nu}(\alpha) = \int I_{\nu\nu}(S\alpha)
\]

Rodgers and walshaw (1966), hereafter referred to as RW, have critically examined the accuracy of this approximation for \( S = 1.66 \), and have concluded that the maximum relative error introduced into the cooling rate is about 1.5 percent.

The absorption coefficient \( k_\nu \) is

\[
k_\nu = S f(\nu - \nu_0)
\]

where \( S \) is the line intensity and \( f(\nu - \nu_0) \) is a line shape factor. Line shape is a net result of natural, collisional, and Doppler broadening, but at atmospheric densities only the latter two are important. A Lorentz line is defined by

\[
f(\nu - \nu_0) = \frac{1}{\pi} \frac{\alpha_L}{(\nu - \nu_0)^2 + \alpha_L^2}
\]

where \( \alpha_L \) is the half-width at half-maximum of the collision broadened line. The Doppler line is defined by

\[
f(\nu - \nu_0) = \frac{\sqrt{\ln 2}}{\alpha_D \sqrt{\pi}} \exp \left\{ - \left( \frac{\nu - \nu_0}{\alpha_D} \right)^2 \ln 2 \right\}
\]
where $\alpha_D$ is the Doppler half-width,

$$\alpha_D = \frac{\nu_0}{c} \left( \frac{2 kT \ln 2}{m} \right)^{1/2} \quad (10)$$

$K$ is Boltzmann's constant and $m$ is the molecular weight. The net effect of both the collisional and Doppler processes is represented as a convolution of the Doppler profile onto the Lorentz profile (Van de Hulst, 1944),

$$f(v-v_0) = \frac{\sigma}{\alpha_D} \left[ \frac{\ln 2}{\pi^{1/2}} \right]^{1/2} \int_{-\infty}^{\infty} \frac{\exp \left( -y^2 \right) dy}{\gamma^2 + (x-y)^2} \quad (11)$$

where

$$\sigma = \frac{\alpha_L}{\alpha_D} \sqrt{\ln 2} \quad (12a)$$

$$x = \frac{v-v_0}{\alpha_D} \sqrt{\ln 2} \quad (12b)$$

$$y = \frac{v'-v_0}{\alpha_D} \sqrt{\ln 2} \quad (12c)$$

$\sqrt{\ln 2}$ being the Lorentz line center corresponding to each position on the Doppler broadened line (Penner, 1959). This is the so-called Voigt profile. At high pressures $\alpha_L$ is large compared to $\alpha_D$, and the profile is essentially Lorentzian, while at lower pressure $\alpha_L \ll \alpha_D$, and the profile is essentially gaussian. Numerical evaluation of each of these profiles indicates that the Voigt profile is roughly coincident with the Lorentz profile at 30km and with the gaussian profile at 70km. At
intermediate heights the line is approximately a strong Doppler core with broad Lorentz wings (Kuhn, 1966).

At tropospheric pressures numerous band models can be used to effectively eliminate the task of evaluating the absorption co-efficient of many overlapping lines at each frequency. Although the Lorentz profile may not be the best representation of a pressure broadened $\text{CO}_2$ line (Bignell et al., 1963), it does allow the Elsasser and quasi-random models to be evaluated conveniently. A complete discussion of band models can be found elsewhere (Goody, 1964a; Kondratyev, 1969). Suffice it to say that most of them are considerably complicated by Doppler broadening. The quasi-random model, for example, still necessitates the evaluation of the Voigt integral (11).

III. Previous work

The techniques used by authors who have addressed the problem of $\text{CO}_2$ cooling in the upper atmosphere are briefly summarized in Table 1. A direct comparison of their results is not strictly possible because of the different temperature profiles used. In any case, the grossest features of the cooling profiles are a trend toward maximum cooling at the stratosphere, with decreased cooling and eventually heating in the mesosphere, (Fig.1).

The results of Drayson (1967) and Kuhn (1966) are probably the best available to date, and their results are in excellent agreement at all levels. Kuhn formulated a quasi-random model from the spectral data computed by Stull et al. (1963), while Drayson integrated directly over the breadth of the $15\mu$ band. Plass's numbers are also in good agreement with these, and this could perhaps be considered phenomenal since Plass's
Table 1

Computations of carbon dioxide cooling in the upper atmosphere

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Region</th>
<th>Transmission Function</th>
<th>Temperature Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curtis and Goody (1956)</td>
<td>49-118 km</td>
<td>Single line</td>
<td>Rocket Panel (1952)</td>
</tr>
<tr>
<td>Plass (1956)</td>
<td>0-75 km</td>
<td>Laboratory measurements</td>
<td>Rocket Panel (1952)</td>
</tr>
<tr>
<td>Ohring (1958)</td>
<td>Tropopause-55 km</td>
<td>Extrapolation of empirical formula of Callendar</td>
<td>&quot;Extrapolation, miscellaneous measurements and theoretical reasoning&quot;</td>
</tr>
<tr>
<td>Murgatroyd and Goody (1958)</td>
<td>30-90 km</td>
<td>Statistical</td>
<td>Compilation of Murgatroyd (1957)</td>
</tr>
<tr>
<td>Young (1964)</td>
<td>0-100 km</td>
<td>Quasi-random</td>
<td>U.S. Standard Atmosphere</td>
</tr>
<tr>
<td>Leovy (1964)</td>
<td>20-80 km</td>
<td>Single line</td>
<td>(Radiative eq.)</td>
</tr>
<tr>
<td>Kondratyev (1965)</td>
<td>30-100 km</td>
<td>Single line</td>
<td>Rocket Panel ARDC-1959 CIRA-1961</td>
</tr>
<tr>
<td>Drayson (1967)</td>
<td>40-110 km</td>
<td>(Frequency integration across band)</td>
<td>U.S. Standard Atmosphere</td>
</tr>
<tr>
<td>Kuhn and London (1969)</td>
<td>30-100 km</td>
<td>Quasi-random</td>
<td>U.S. Standard Atmosphere and others</td>
</tr>
</tbody>
</table>
transmission functions were based on the experimental data of Cloud (1952) extrapolated to low pressures and short path lengths.

Young (1964) obtained extraneously large cooling rates which he attributed to an improper formulation of the transmission function. The variation of Curtis's and Murgatroyd's results probably can be attributed to the temperature data used.

An important implication of these results that has been suggested before (Kuhn, 1971; RW, 1966) is that cooling rates in the middle stratosphere are relatively insensitive to the band model used. The results of the present calculation also substantiate this possibility.

IV. The transmission function

Calculations of infrared cooling rates must necessarily depend upon band models to represent averages over the small scale structure of a band; that is, as long as it remains impossible to accurately measure the absorption co-efficient as a function of frequency, or to theoretically specify the structure of an absorption band in some manageable form. Numerous empirical relations have been derived from laboratory measurements of gaseous absorption, but these can tolerate only a limited variation of pressure, temperature and mass path. An interesting comparison of some empirical transmission functions is reproduced in Table 2.

Motivated by the complexity of theoretical models in the presence of Doppler broadening and the inapplicability of empirical formulations at low pressures, we have formulated a transmission function which utilizes the approximation of non-overlapping lines, and is capable of treating Doppler broadening with complete simplicity.
<table>
<thead>
<tr>
<th>Investigator</th>
<th>Form of data</th>
<th>Temperature</th>
<th>Max. usable height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloud (1952)</td>
<td>experimental curves of transmission</td>
<td>room</td>
<td>50 mb</td>
</tr>
<tr>
<td>Howard et al. (1956)</td>
<td>experimental curves and empirical fit</td>
<td>room</td>
<td>300 mb.</td>
</tr>
<tr>
<td>Burch et al. (1962)</td>
<td>experimental curves and empirical fit</td>
<td>room</td>
<td>40 mb.</td>
</tr>
<tr>
<td>Yamamoto and Sasamori (1958)</td>
<td>curves of calculated transmission and</td>
<td>218°, 240°</td>
<td>16 mb.</td>
</tr>
<tr>
<td></td>
<td>empirical fit</td>
<td>265°, 300°</td>
<td></td>
</tr>
<tr>
<td>Stull, Wyatt and Plass (1963)</td>
<td>tabulation of calculated transmission</td>
<td>200°, 250°</td>
<td>20 mb.</td>
</tr>
<tr>
<td></td>
<td>values</td>
<td>300°</td>
<td></td>
</tr>
</tbody>
</table>

* from Rodgers (1964)
A. The 15\(\mu\) bands

Absorption in the 500-860 cm\(^{-1}\) region is due primarily to the fundamental and fourteen sub-bands of \(^{12}\text{C}_16\text{O}_2\), \(^{13}\text{C}_16\text{O}_2\), \(^{12}\text{C}_16\text{O}_{18}\), \(^{12}\text{C}_16\text{O}_{17}\), and \(^{13}\text{C}_16\text{O}_{18}\), (Drayson and Young, 1967). Each band consists of an intense Q branch (\(\Delta J=0\)) and regularly spaced P and R-branches. (\(\Delta J=-1\) and \(\Delta J=+1\), respectively, where \(J\) is the rotational quantum number.) Young (1964) has computed the position and intensity of each of 982 strong lines and 1008 weak lines for six temperatures between 175 and 300°K. These data are employed exclusively in the present computation.

B. The single line approximation

The degree to which the spectral lines in an interval overlap is a function of the Lorentz half-width and absorber amount as well as of the spacing of the individual lines. There will be negligible overlap for absorption occurring in the linear law regime for sufficiently wide line spacing since the absorption occurs primarily in the core of the lines. On the other hand absorption occurring in the square root region will be determined by the growth of the Lorentz wings, and overlap can occur even for widely spaced lines. A necessary condition for the validity of the single line approximation is therefore

\[
\bar{A} \ll 1
\]  

(13)

where \(\bar{A}\) is the mean absorption of the band. (Goody, 1964a). A sufficient condition can be determined only from direct analysis of the lines in the CO\(_2\) spectrum.
The most obvious features of Young's data are the occurrences of randomly overlapped P and R-branches with a mean line spacing of 1.55 cm\(^{-1}\), and widely spaced groups of Q-branch lines with a mean line spacing of 0.01 cm\(^{-1}\). Shved (1964) has computed the functions

\[
\frac{\partial}{\partial z} A(z, z') \quad \text{and} \quad \frac{\partial^2}{\partial z^2} A(z, z')
\]

where \(A(z, z')\) is the absorptivity between \(z\) and \(z'\), for various regions of the CO\(_2\) spectrum. The results indicate that the single line approximation would produce a maximum error in the flux divergence of several percent in the P and R-branches above 25km. The approximation could be used in the Q-branches with similar error above 30-35km, except in the crowded interval 667-672 cm\(^{-1}\) where it could be used only above 50km. This computation uses the single line approximation for all regions of the CO\(_2\) spectrum and all mass paths above 30km, and the error incurred by the use of this approximation should be small. Unfortunately, this formulation prohibits the computation of transmission between levels above 30km and those below this level, since most of the absorption will then be occurring in regions of strong overlap.

C. Regions of importance for Doppler broadening.

The Lorentz wings on a Voigt profile begin at the point defined by

\[
\frac{S \alpha_L}{\pi (\nu^2 + \alpha_L^2)} = \frac{S}{\alpha_L \sqrt{\pi}} \exp \left( -\frac{\nu^2}{\alpha_L^2} \right)
\]

(RW, 1966). \(S\) is the line intensity and \(\nu\) is the distance from the line center. Strictly speaking, Doppler broadening should be considered above the level where \(\alpha_L = \alpha_D\) or about 10mb, using Eq. (15). Under
certain conditions, however, Doppler broadening can be ignored in strong lines up to a height of 50km (Plass and Fivel, 1953). The reasoning behind this is essentially that the absorption in a strong Voigt line is due to the growth of the broad Lorentz wings rather than the saturated Doppler core, so that even if $C_L \ll C_D$, the line can be treated as pure Lorentzian. Similarly, the absorption of very weak lines will follow the linear law, which is entirely independent of line shape. The combined effect of Doppler and Lorentz broadening then need only be considered for lines of intermediate strength. The strong lines in the CO$_2$ spectrum are located mostly at the center of the band and the weak lines at the edges, so it is for the lines in the intermediate region that the Voigt function must necessarily be calculated.

D. Absorption of the mixed line.

Evaluation of the absorption co-efficient over the Voigt profile (11) is not a straightforward problem. Analytic solutions are not available, although some asymptotic methods have been proposed (Van Trigt, 1968). These appear to be as unmanageable as the Voigt integral itself. Typically, the convergence of numerical solutions of (11) depends on the ratio $C_L/C_D$ and the distance from the line center, so that no one quadrature technique is valid everywhere. This work has utilized the method of Shved and Tsaritsyna (1963). Although the method is extremely accurate, it is too time consuming for routine use.

An extremely simple formulation of the absorption of a non-overlapping Voigt line is due to Curtis (RW, 1966). Consider the equivalent width, $W$,.
defined by

\[ W = \int_{-\infty}^{\infty} (1 - e^{-kn}) d\nu \]  \hspace{1cm} (16)

The solution to this equation for a Lorentz line is the familiar Ladenberg-Reiche formula,

\[ W_L = 2\pi x_0 \mu e^{-\mu} \left\{ I_0 (\mu) + I_1 (\mu) \right\} \]  \hspace{1cm} (17)

where

\[ \mu = \frac{Sa}{2\pi x_0} \]  \hspace{1cm} (18)

\( a \) being the absorber amount, and \( I_0 \) and \( I_1 \) being Bessel functions of the first kind with imaginary arguments. For a pure Doppler line,

\[ W_D = x_0 \int_{-\infty}^{\infty} \left\{ 1 - e^{\nu (\omega - \lambda)} \right\} d\lambda \]  \hspace{1cm} (19)

where

\[ \omega = \frac{Sa}{x_0 \sqrt{\pi}} \]  \hspace{1cm} (20)

The equivalent width of a weak line is independent of line shape and is written

\[ W_w = Sa \]  \hspace{1cm} (21)
Curtis has suggested that the equivalent width of the mixed line could be written with reasonable accuracy as

$$W_M = W_L + W_D - \frac{W_L W_D}{W_W} \tag{22}$$

Although this approximation has no theoretical derivation, it is arrived at by the following empirical argument (Curtis, private communication).

To a first approximation the Voigt profile is simply the obliteration of the broad Lorentz profile by a narrow gaussian profile, and a reasonable combination of the two profiles would meet the following requirements:

$$\begin{align*}
W_{L,\text{max}} &< W_M < W_W \tag{23a} \\
W_{D,\text{max}} &< W_M < W_W
\end{align*}$$

$$\begin{align*}
W_M &\rightarrow W_{L,\text{max}} \quad \text{as} \quad \frac{W_L}{W_D} \rightarrow 0 \tag{23b} \\
W_M &\rightarrow W_{D,\text{max}} \quad \text{as} \quad \frac{W_L}{W_D} \rightarrow \infty
\end{align*}$$

and $W_M$ is a smooth function of absorber amount $a$ and half-width ratio $\alpha_L/\alpha_D$.

(23a) follows from the fact that both $W_L/W_W$ and $W_D/W_W$ always lie between 0 and 1. (23b) follows in the case where $W_L/W_D \rightarrow 0$ from
\[ \frac{W_M - W_D}{W_D} = \frac{W_L}{W_D} \left( 1 - \frac{W_D}{W_W} \right) < \frac{W_L}{W_D} \]  

(24)

and in the case where \( W_D/W_L \to 0 \) by symmetry. The continuity property ensures finite flux divergences.

Each of these properties is shared by the true equivalent width of the Voigt line, \( W_V \), and this fact is sufficient to ensure that \( W_V \) and \( W_M \) should be very close to each other for fixed values of \( \lambda_L/\lambda_D \).

The accuracy of this approximation is illustrated in Figures 2 through 5 in which \( W_V \) and \( W_M \) and their derivatives with respect to path length are plotted as functions of the parameter

\[ k_o a = \frac{Sao}{\lambda_D} \sqrt{ \frac{ln^2}{\pi} } \]

for two values of \( \lambda_L/\lambda_D \).

The solid line in each case indicates values obtained from numerical integration of the mixed Doppler-Lorentz profile, while the dotted lines indicate those obtained from Eq. 22.

At values of \( \lambda_L/\lambda_D \) roughly corresponding to the lower stratosphere, \( W_M \) is about 4 percent greater than \( W_V \) for weak absorption and 20 percent greater for strong absorption. The error in the derivative \( \partial W/\partial a \) is a minimum at the extrema of the curve, and is a maximum of 25 percent for intermediate strength absorption. For a value of \( \lambda_L/\lambda_D \) roughly corresponding to the stratopause, the approximate and exact expressions are identical for weak absorption, but deviate rapidly from each other at longer path lengths. The plot of \( \partial W/\partial a \) demonstrates the serious nature of this problem. The two formulations are equal over
a large range of weak absorption, but differ by a factor of two for strong absorption. Since the cooling rate at a given level is directly proportional to the flux divergence at that level, the cooling due to the strong lines of the CO$_2$ band will be grossly overestimated by the Curtis approximation. This sets an effective upper limit of about 55 km on the height at which this approximation is useful. Above that height the Lorentz contribution to the Voigt profile of strong lines is overestimated, and unreasonably large absorption occurs.

E. Band transmission.

The equivalent width of an array of $N$ non-overlapping lines is simply given by

$$W_{\text{band}} = \sum_{i=1}^{N} W_i$$  \hspace{1cm} (25)

and the mean transmission over some finite band width $\Delta$ is

$$T = 1 - \frac{W_{\text{band}}}{\Delta}$$  \hspace{1cm} (26)

The Curtis model can be applied to the entire 15 $\mu$m band by using a technique similar to the one used by Wyatt et al. (1962) to formulate the quasi-random model. The spectral data of Young are grouped into 5 cm$^{-1}$ intervals, corresponding roughly to the resolution of the wide slit spectrometer. The lines within each 5 cm$^{-1}$ interval are then grouped into intensity decades, or groups of lines whose intensities fall within a factor of ten of each other. A mean intensity is then computed for
each of the top five decades, and the equivalent width of each decade is represented as the product $\alpha \overline{W}$, where $\alpha$ is the number of lines in the decade and $\overline{W}$ is the width of the mean line.

Figures 6 through 8 are CO$_2$ spectra computed in this manner. The pressures and path lengths are chosen so that a direct comparison can be made with the results of Burch et al. (1962), and with the quasi-random formulation of Kuhn (1966). Qualitatively the agreement in both cases is most remarkable. All of the major features observed experimentally (Fig. 9) and computed by Kuhn are well reproduced by the single line formulation, with the single exception of the sharp peak at 655 cm$^{-1}$ that was smoothed out by the averaging process. Although it is difficult to obtain precise quantitative information from experimental measurements of weak absorption, Table 3 is a comparison of the integrated absorption $\int A_0 d\nu$ of Burch et al. and the total equivalent width computed from the single line approximation. The limits of integration are slightly different for the two numbers, but this should make little difference since absorption by the wings is small at these mass paths. The single line approximation in each case gives less absorption than is actually observed. If the accuracy of the measurements is not questioned, there are two possible interpretations of this discrepancy. Most of the absorption at these pressures is occurring at the peak of the 15 $\mu$ band which is densely populated with Q-branch lines. The difference in the absorption can then be interpreted as a measure of the accuracy of the single line approximation in this region of the spectrum. Alternatively, the Curtis approximation to the Voigt line profile should give a greater integrated absorption if it gives any difference at all. An important
### Table 3

Comparison of theoretical and experimental absorption

<table>
<thead>
<tr>
<th>Mass Path (atm cm)</th>
<th>Pressure (mm)</th>
<th>$\int A_\nu d\nu_{495}$</th>
<th>$W_{506-856}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.32</td>
<td>6.24</td>
<td>16.9</td>
<td>12.9</td>
</tr>
<tr>
<td>0.69</td>
<td>1.89</td>
<td>6.5</td>
<td>4.4</td>
</tr>
<tr>
<td>0.24</td>
<td>0.65</td>
<td>4.0</td>
<td>1.9</td>
</tr>
<tr>
<td>5.73</td>
<td>15.6</td>
<td>34.6</td>
<td>30.2</td>
</tr>
</tbody>
</table>
implication of the smaller integrated absorptions observed experimentally might be that the Voigt profile is not the best approximation of a CO$_2$ line undergoing both pressure and Doppler broadening. Having seen that the Lorentz profile is not an ideal profile for CO$_2$ lines to begin with, the inappropriateness of the Voigt profile is indeed a possible explanation.

The single line transmission function is plotted in Figure 10 along with an empirical transmission function and the statistical model. The single line model agrees well with the statistical model fitted to the weak lines of the CO$_2$ band, and the discrepancy between these and the other models at long path lengths indicates the substantial degree to which the CO$_2$ lines overlap in strong absorption.

V. Calculation of infrared cooling rates

A. Cooling to space

RW (1966) has suggested that the radiative cooling problem can be enormously simplified by considering only the term in the radiative transfer equation that represents direct communication to space. This eliminates
the complicated exchange terms between the different levels and includes only the black body flux at the level in question. The cooling can then be written,

\[
C(z, \Delta \nu) = \frac{dT_{\Delta \nu}(z, \infty)}{dz} \cdot B_{\Delta \nu}(z) \quad (27)
\]

These authors have shown this approximation to be adequate under most circumstances, except in the presence of a discontinuity in the temperature gradient.

B. Source function.

The breakdown of local thermodynamic equilibrium (LTE), grossly complicates the form of the source function at high levels of the atmosphere. In the spirit of Milne (1930), LTE can be defined as a state in which it is possible to define a kinetic temperature \(T\), and in which the emitted radiation is entirely independent of the field of incident radiation. The first condition is satisfied throughout the stratosphere and mesosphere (Spitzer, 1949), and the second will be satisfied only if the vibrational and rotational energy levels are populated according to Boltzmann's law,

\[
\frac{n}{n_0} = \exp\left(-\frac{\hbar \nu}{kT}\right) \quad (28)
\]

where \(n\) and \(n_0\) are the populations of the excited state and ground state, respectively. The emission under such conditions is given by Kirchhoff's law,

\[
f_\nu = \hbar \nu B_\nu(T) \quad (29)
\]
where \( j_\nu \) and \( k_\nu \) are the co-efficients of emission and absorption, and \( B_\nu \) is the Planck function at frequency \( \nu \) and temperature \( T \).

Eq. 28 indicates that the relative populations of the states is a function only of temperature, and therefore a function of the number of collisions that take place at a given level. Molecules will absorb and emit independently of the incident radiation field if there is a sufficient number of collisions to maintain the Boltzmann distribution; otherwise the molecules will radiate according to their own rate of spontaneous emission.

Denoting the natural lifetime of an excited state by \( \phi \) and the collisional relaxation time by \( \gamma \), a necessary condition for the maintenance of LTE is

\[
\gamma \gg \phi \tag{30}
\]

For a given transition \( \phi \) can be computed directly (Goody, 1964a).

\[
\phi = \frac{c^2}{8 \pi \nu^2 S} \tag{31}
\]

where \( S \) is the molecular band intensity and \( c \) is the speed of light. Yamamoto and Sasamori (1958) give \( S = 212 \text{(atm cm)}^{-1} \text{cm}^{-1} \), or \( 2.365 \times 10^{-7} \text{ cm}^{-2} \text{ sec}^{-1} \). This gives a natural lifetime of \( \phi = 0.40 \text{ sec} \).

Determination of the collisional relaxation time \( \gamma \) is a more serious problem, and estimates of its value range from \( 6 \times 10^{-6} \text{ sec} \) (Houghton, 1969) to \( 1.5 \times 10^{-5} \text{ sec} \) (Curtis and Goody, 1956). The relaxation time is inversely proportional to pressure, and

\[
\frac{\gamma (\rho)}{\gamma (\rho_o)} = \frac{\rho}{\rho_o} \tag{32}
\]
The pressure at which $\gamma/\phi = 1$ is then 0.013mb (\(\sim 78\)km) and 0.05mb (\(\sim 70\)km) for the extreme values of $\gamma_0$. LTE therefore holds throughout the stratosphere and mesosphere.

C. Inhomogeneous path approximation.

The variation of the half-width of the mixed line can be treated accurately by the use of the traditional Curtis-Godson approximation. That this is the case was demonstrated by van de Hulst (1945) and Goody (1964b). Taking the cosine transform of the optical path (5),

$$f(t) = \int_{-\infty}^{\infty} \mathcal{V} \cos \nu t \, d\nu$$

(33)

For the Voigt profile,

$$f(t) = \int \exp \left( -\alpha_L t - \frac{1}{4} \alpha_D t^2 \right) \, d\alpha$$

(34)

Over an inhomogeneous path this is to be approximated by some effective absorber amount $\tilde{a}$ and some effective line widths $\tilde{\alpha}_L$ and $\tilde{\alpha}_D$,

$$f(t) = \tilde{S} \tilde{a} \exp \left( -\tilde{\alpha}_L t - \frac{1}{4} \tilde{\alpha}_D t^2 \right)$$

(35)

When the exponentials in (34) and (35) are expanded in a power series and the coefficients of like powers of $t$ are equated, the zero and first order terms yield the classical Curtis-Godson approximations,

$$\tilde{S} \tilde{a} = \int S \, d\alpha$$

(36)
and

\[ \tilde{I}_{\tilde{a}} \tilde{a}_{\tilde{L}} = \int S \alpha_{\tilde{L}} d\alpha \]  \hspace{1cm} (37)

The co-efficients \( \alpha_{D} \) and \( \alpha_{P} \) do not appear until second order. Eq. 10 indicates that \( \alpha_{D} \) varies by a maximum of 26 percent over the range of temperatures encountered in the stratosphere and mesosphere so that \( \alpha_{D} \) is effectively constant, and \( \tilde{\alpha}_{D} = \alpha_{D} \). Stated otherwise, if the Voigt profile is considered to be superposed Doppler and Lorentz profiles, the variation of its shape can be attributed to the variation of the Lorentz wings provided that the contribution from the Doppler core is held fixed.

In the cooling to space model,

\[ \tilde{\alpha}_{\tilde{C}} = \frac{\alpha_{\tilde{C}}(0)}{2} \frac{P}{P_0} \]  \hspace{1cm} (38)

D. Absorber amount.

The volume mixing ratio of CO\(_2\) is a constant 320 ppm up to 70km, where dissociation is thought to then occur, (Hays and Olivero, 1970). Martell (1970) had made measurements in the height range 44-62km and has verified a constant mixing ratio of 322ppm.

E. Numerical methods.

Although the Ladenberg and Reiche function (17) is expressed in terms of Bessel functions with imaginary arguments, this function is more
conveniently represented as a series of weighted Chebyshev polynomials. Writing the Ladenberg-Reiche function as,

\[ f(\mu) = \mu e^{-\mu} \left\{ I_0(\mu) + I_1(\mu) \right\} \]  

(39)

Rodgers and Walshaw (1963) have shown that this can be approximated by

\[ f(\mu) \approx \mu \sum_{n=0}^{3} (\mu - 0.5)^n a_n \]

for \( 0 \leq \mu \leq 1 \)  

(40)

with a maximum error of \( 1.5 \times 10^{-4} \). And

\[ f(\mu) \approx \sqrt{\mu} \sum_{n=0}^{4} b_n \left( \frac{1}{\mu} - 0.5 \right)^n \]

for \( \mu > 1 \)  

(41)

with a maximum error of \( 1.0 \times 10^{-4} \). The standard series solution for the non-overlapping Doppler line is poorly convergent for intermediate values of absorber amount, and also is more efficiently evaluated in terms of a Chebyshev expansion. For

\[ f(\mu) = \int_{-\infty}^{\infty} \left( 1 - \exp[\mu e^{-x^2}] \right) dx \]  

(42)

the polynomial expansion is

\[ f(\mu) \approx \mu \sqrt{\pi} \sum_{n=0}^{7} b_n \mu^n \]

for \( \mu \leq 4.2 \)  

(43)

with a maximum error of \( 1.0 \times 10^{-5} \). And

\[ f(\mu) \approx \sqrt{\ln \mu} \sum_{n=0}^{6} c_n \left( \frac{1}{\ln \mu} - 0.36 \right)^n \]

for \( \mu > 4.2 \)  

(44)
with a maximum error of $1.0 \times 10^{-5}$ (Rodgers, 1964). The co-efficients used in the summations are given in Appendix I.

Cooling was computed at equally spaced intervals of $\log_{10} p_{\text{mb}}$ from 30 to 60km. A five point centered differentiation formula was used to compute derivatives of the transmission function.

VI. Discussion of results.

The cooling rate profile computed for the 1962 Standard Atmosphere temperatures is illustrated in Figure 1. The results indicate a cooling of 1.4 degrees per day at 30km and a maximum of 4.8 degrees per day near 60km. These agree relatively well with previous calculations, although near 40km the rates are slightly smaller than any of the others. A direct comparison can be made with the results of Kuhn and London and of Drayson, both of which were also obtained from the Standard Atmosphere's temperature profile. Their rates are larger at all heights and are a maximum of two degrees per day greater at 50km.

The present calculation is necessarily terminated at 60km because above this height Curtis's approximation gives excess cooling from the Lorentz wings of the lines. A more realistic estimate of the cooling above this height could be obtained by considering a pure Doppler profile, although non-LTE effects must also be included above 75km.

There are two possible reasons for the smaller cooling rates in the vicinity of the stratopause. Firstly, the spectral data used in the calculation may underestimate the net absorption of the $15\mu$ band. Young's data were revised once (Drayson, 1967) and are currently being revised
again (Drayson, private communication). The intensity of some sub-bands has been increased, but the net result is likely to be small. A second and more probable cause is that the cooling to space approximation is inappropriate near the stratopause. RW compared cooling to space and total cooling at 1mb and observed a maximum difference of 1.4 degrees per day, which is comparable to the present results.

VII. Summary and conclusions.

An extremely simple procedure for computing radiative cooling in the middle and upper stratosphere has been examined. The technique ignores the effect of line overlap, and sidesteps the complications of the Voigt line profile by computing the equivalent width approximately with a formula suggested by Curtis. Non-overlapping lines appears to be an excellent approximation except perhaps at the peak of the 15μm band, and even there the error is small. Curtis's approximation is adequate for weak and intermediate lines or when there is a large Lorentz component in the Voigt profile. The formula appears to be inaccurate for very strong lines that are essentially Doppler in character.

Excellent qualitative agreement with the experimental results of Burch et al. is obtained. Their spectroscopic measurements show a slightly greater integrated absorptance than the calculated spectra and a possible explanation may lie in the use of the single line approximation, or more significantly, from the assumption of a Voigt line profile.

A sample cooling rate profile is computed from the cooling to space approximation which ignores the exchange of radiation between the various atmospheric layers. The most detailed calculation of cooling in this
height region appears to be Kuhn's, and the agreement with his results is
good in the middle stratosphere, but is poorer near the stratopause where
the present cooling rates are somewhat smaller.

The technique outlined in this work is probably adequate for most
purposes, providing a great deal of accuracy is not required. Its
accuracy can be greatly increased by eliminating the cooling to space
approximation and computing the contribution from each layer. This
would, however, entail the smooth joining of the single line transmission
function with some band model that conveniently treats overlap, such as
the quasi-random model. With such a fit the Curtis approximation will
probably yield accurate enough results for energy budget calculations up
to 55km.
### Appendix I

#### Coefficients for polynomial expansion

**A. Ladenberg-Reiche function**

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<th>(b_n)</th>
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**B. Doppler line absorption**

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<th>n</th>
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REFERENCES


Curtis, A.R. (1972), Private communication.


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Figure 1 - Comparison of CO$_2$ cooling rate profiles computed by different authors. Curves are labelled as follows: L - Leovy (1965); P - Plass (1956); M - Murgatroyd and Goody (1958); C - Curtis and Goody (1956); Y - Young (1964); KL - Kuhn and London (1969); D - Drayson (1967); K - Kondratyev (1965); H - This calculation.
Figure 2 - Curve of growth of the mixed Doppler-Lorentz line computed from the approximation (22) and from numerical evaluation of the Voigt integral (11).
Voigt formula

Curtis\' approximation

Figure 3 - Curve of growth of the mixed Doppler-Lorentz line computed from the approximation (22) and from numerical evaluation of the Voigt integral (17).
Figure 4 - A comparison of $\partial w(a)/\partial a$ for $W_M$ evaluated with Curtis's formula and $W_V$ obtained by numerical integration. Ordinate is $\log_{10} dw/d(k_o a)$. Half-width ratio of 1.9 corresponds roughly to $Z=25$ km.
Figure 5 - A comparison of $\partial w(a)/\partial a$ for $W_M$ evaluated with Curtis's formula and $W_V$ obtained by numerical integration. Ordinate is $\log_{10} dW/d(k_0 a)$. Half-width ratio of 0.04 corresponds roughly to $Z=53$ km.
Figure 6 - CO$_2$ spectra computed from the single line model with Curtis's approximation. The spectra are in excellent agreement with those computed by Kuhn (1966) using the quasi-random model.
Figure 7 - CO₂ spectra computed with the single line model and Curtis's approximation.
Figure 8 - CO₂ spectra computed with the single line model and Curtis's approximation.
Figure 9 - CO$_2$ spectra measured by Burch et al. (1962).
Figure 10 - Comparison of transmittance curves obtained with empirical data and band models.
SL - Single line approximation (this work); E - Experimental data (RW, 1966); HR - Statistical
(Murgatroyd and Goody, 1958; RW, 1966); W - Statistical, weak lines; S - Statistical, strong lines (Murgatroyd and Goody, 1958; RW, 1966).